CLOSEABLE GLASS CONTAINER COMPRISING A PLASTIC COATING APPLIED BY INJECTION MOLDING AND METHOD FOR THE PRODUCTION THEREOF

The invention is based on a closeable glass container comprising a plastic coating applied by injection molding according to the features of the preamble of Claim 1.

The invention is further based on a method for the production of the container comprising a coating applied by injection molding.

Glass containers of this type comprising a coating applied by injection molding are used for medical purposes in particular, but they are also used for cosmetic purposes or to store food and beverages. The purpose of these plastic coatings, for example, is to hold glass splinters together if the coated glass container breaks. The plastic coating therefore also serves to provide protection against bursting and/or shattering.

Glass containers of various species comprising a plastic coating applied in different fashions using the most diverse types of plastics have been made known in numerous publications.

In DE-OS 24 31 952 it was made known to coat glass bottles with a plastic that comprises a thermosetting resin that is softened before use, either by means of internal plasticizers, i.e., by means of substances that react during production of the thermosetting plastic and thereby become part of the resin, or by means of external plasticizers that are added to the finished resin in suitable fashion. The softened, thermosetting resin is available as coating powder, is ground to a

specified particle size, and then applied electrostatically to the bottles. The application of the powder can also take place by means of immersion in a fluidized bed or in an electrostatic fluidized bed. The applied layer is then cured, preferably in an infrared oven. In this known case, the coating of the bottles therefore takes place using the method of powder coating on a thermosetting basis that does not allow for an exact contour of the bottle comprising a coating applied by injection molding, as required, for example, to shape the base section with regard for the stability of the glass bottle, and which is also relatively costly.

Furthermore, the softened thermosetting resin cannot be applied to the glass bottles using the technique of injection molding, because this technique requires that a plastic molding compound be available that can be softened under the influence of heat, so that it can then be pressed into the molding die. By definition, thermosetting plastics are not capable of being heat-softened, however.

To the extent that glass containers have been put into concrete terms in the publications about the related art, containers such as beer bottles, mineral water bottles, cosmetic containers and the like are typically named. Additionally, the principle of coating glass containers by injection molding is also used with a special species of containers, namely closeable medical containers subject to a relatively high pressure, especially pressure containers than can be filled under pressure with medically effective substances and a propellant, and the opening of which is closeable using a delivery element, in particular a metering valve. In conjunction with a dispensing head that interacts with the delivery element in such a fashion that the delivery element is actuated when both parts are pressed together and a certain quantity of the medically effective substance is released through a spray opening as aerosol, these products serve as applicators for medical applications, in particular for patients with asthma or other bronchopathies.

The use of pressure containers made of metallic materials for such applicators is known. The protection against bursting and/or shattering in pressure containers of this type is achieved by means of the properties of the selected material that are advantageous in this regard (high toughness, high strength).

A disadvantage of these pressure containers, however, is that the non-transparent pressure container makes it impossible to visually determine how much of the substance to be released remains inside. This is a particular disadvantage when it comes to dispensing inhalants that often have the character of an emergency remedy (e.g., asthma preparations). Without a visual check, the risk exists that the pressure container could be empty when an emergency arises.

Additionally, a pressure container in the form of small glass bottles was made known in DE-AS 11 08 383. The capacity of the small bottle can be 5 to 50 ml. The release opening is located on the top end of the bottle. This is usually closed by inserting the delivery element, e.g., a metering valve having a usually cylindrical cannula projecting upward, into the pressure container or crimping it on the pressure container, often using an elastic seal between head and metering valve. The pressure container is thereby subjected to a relatively high internal pressure.

The known pressure container made of glass is covered with a coating of a transparent plastic that is sprayed on or applied via immersion, with the exception of the rim, to which the metering valve is crimped. This coating comprises a flexible soft plastic, e.g., PVC, having high expansion. The high expansion is important, because, if the glass container bursts, the high internal pressure acts on the soft plastic. If the soft plastic would not be able to *[words missing]* by means of a deformation of the coating, e.g., by means of *[words*

missing], a sudden destruction of the soft plastic resulting from chemical attack would be expected.

Since the pressure container is comprised of a transparent material (glass) and the plastic sheathing is transparent, this known pressure container has the advantage that it makes it possible to visually determine how much of the substance to be released remains inside.

A disadvantage of the known pressure container, however, is the fact that the transparent pressure container made of glass—despite its plastic coating—is not safe enough in case of explosion, e.g., caused by improper handling, because a coating is not applied in the region of the metering valve, or because, generally speaking, if bursting occurs, the plastic sheathing can expand and burst like a balloon, which causes parts of the glass container to spray rapidly into the surroundings, including the metering valve in particular, which can come loose from the rim to which it was crimped.

Within the framework of the production of the final pressure container, the plastic layer that provides protection against bursting and shattering is applied directly to the glass pressure container in the simplest fashion possible—i.e., not by means of immersion or spraying—by coating this with an extruded plastic in a molding die. A concept of this type was made known in FR 2 631 581 B1. This publication describes a small glass bottle having a tapered neck section that can be filled under pressure with a substance sprayable as aerosol and a propellant, the opening of which is closeable using a delivery element, and that comprises a plastic coating applied by injection molding.

In the known case, the glass pressure container comprises a small bottle having a cylindrical neck section, and the molding die is designed so that a plastic coating is also applied by injection molding to the neck section flush with the

opening of the small bottle. When the neck section of the small glass bottle is designed in this fashion, however, attachment of the delivery element—the metering valve—is not without problems. Furthermore, the plastic coating coats the small glass bottle completely. If bursting occurs, the coating can partly expand and burst and therefore lose its property of providing protection against bursting and shattering. The aforementioned publication furthermore makes no statement about the type of plastic material; it is therefore not considered to be essential in terms of function.

A further example of the aforementioned concept was made known in DE 196 32 664 A1. It discloses a small glass bottle having a tapered neck section that is fillable under pressure with a substance sprayable as aerosol and a propellant, the opening of which is closeable using a delivery element, that comprises a plastic coating applied by injection molding, and that is designed so that a secure attachment of the delivery element and a reduction of the wall thickness of the small glass bottle is possible and, on the other hand, the protection against bursting and shattering is increased considerably compared to the container made known in the FR publication. This known small bottle also comprises the following features:

- the neck section comprises a sealing rim designed in the shape of a bead on the side where the opening is located for the mechanical attachment of the delivery element, which also comprises a plastic coating applied by injection molding,
- a plurality of pressure-compensating openings designed in the shape of holes is formed in the plastic coating of the glass body applied by injection molding,
- the coating is composed of an elastic plastic material having distinct shrinkage, and it is shrunk on the small glass bottle.

Due to the sealing rim designed in the shape of a bead, a secure and permanent mechanical attachment of the delivery element is possible. Since the plastic coating also covers the glass sealing rim, the delivery element is still held mechanically even if the glass body bursts, which increases the protection against bursting. The pressure-compensating openings prevent the plastic coating from expanding and bursting, which also greatly increases the protection against bursting and shattering.

If bursting occurs, the filled substance and the propellant can escape through these pressure-compensating openings. Furthermore, due to the fact that the contents of the glass container can escape, the risk that the filled substance will chemically attack the coating material, e.g., by means of stress corrosion cracking, is further reduced, which further reduces the risk of bursting.

By using an elastic plastic material having distinct shrinkage, it was found that the ability of the small glass bottle coated by injection molding to be pressure-loaded is higher than the ability of the pure glass bottle to be pressure-loaded, by many times over. This effect makes a thinner wall thickness of the small glass bottle possible. The elasticity of the plastic material thereby offsets the shrinkage.

The invention is based on a glass container of this type.

In the known case, specially designed small glass bottles, “glass inlets”, are coated with a transparent plastic using the conventional injection-molding system. Since relatively viscous thermoplastics are typically used as plastic material in the conventional injection-molding system, very high injection pressures (approx. 300 bar) occur during injection molding, which can easily destroy the glass inlet. This destruction results in a high percentage of waste. Additionally, the productivity of a manufacturing system is greatly reduced. For this reason, limits are also placed on the reduction of the wall thickness of the

glass inlets. The same applies for inlets made of a thermolabile plastic, especially a thermoplastic material.

Moreover, the known glass containers comprising a coating applied by injection molding cannot be sterilized by means of autoclaving using superheated steam at 121° C for a period of 20 minutes. A sterilization method of this type is typically required for containers used for medical purposes, however.

The invention is based on the object of developing the closeable glass container of the type initially described, which comprises a plastic coating applied by injection molding, and to carry out the method for its production in such a fashion that, despite the thin walls of the glass container, it is possible to reduce the waste produced during injection molding considerably, and the containers comprising a coating applied by injection molding can be subjected to high temperatures, e.g., during sterilization using superheated steam.

This object is successfully attained according to the invention with regard for the closeable glass container by the fact that the plastic coating comprises at least one reactively-vulcanizing plastic able to be heat-softened, and it is applied in the process of injection molding using the reactive-injection molding technique.

With regard for the method for the production of this glass container having a plastic coating applied by injection molding designed as small glass bottles, the object is successfully attained according to the invention using the steps:

- Production of the entire small glass bottle having base section, cylindrical jacket section, tapered neck section including sealing rim designed in the shape of a bead, according to conventional glass technology,

- Coating of the entire small bottle by injection molding in a mold using at least one reactively-vulcanizing plastic capable of being heat-softened, using the reactive-injection molding system.

When the reactive-injection molding system (RIM system) is used according to the invention, at least one reactively-vulcanizing plastic with low viscosity compared to polymers, e.g., a thermosetting resin, is injected in a mold around the insert—the glass container—at relatively low injection pressures (less than 10 bar) and relatively low mold temperatures.

Since only a low injection pressure is necessary, the thickness of the container walls can be reduced, while reducing waste at the same time. Moreover, the reactively-vulcanizing plastics used are able to be subjected to higher temperatures than the thermoplastics typically used in the conventional injection molding system, such as PP, PE, PET, PS, as a result of which the containers comprising a coating applied by injection molding are capable of being sterilized in autoclaves using superheated steam. The low mold temperatures also make it fundamentally possible to use inlets made of a thermolabile plastic.

Particular advantages are achieved according to one embodiment of the invention using a container developed as a small glass bottle that is capable of being filled under pressure with a substance sprayable as aerosol and a propellant, that comprises a tapered neck section having a sealing rim designed in the shape of a bead integrally molded on the side where the opening is located for the mechanical attachment of a delivery element, by means of which the opening of the small glass container is closeable, and that is encased in the plastic coating in such a fashion that the plastic coating also encases the sealing rim designed in the shape of a bead. Small glass bottles of this type come onto the market in various stages of development. In the basic form, the small glass bottle is supplied without a delivery element installed. A commercial form having

a delivery element installed is also feasible. The small glass bottle can thereby be filled or unfilled. All of these commercial forms use the small bottle according to the invention, however, and are therefore included in the scope of protection.

By using the RIM method, the entire production process used to manufacture the coated container—which is fillable under pressure with a substance sprayable as aerosol and a propellant ("aerosol containers")—can be simplified as well. The following possibilities result, for example:

By introducing different materials at different points in the mold, the material hardness can be increased specifically in the region of the container head in order to improve the quality of the crimping with a metering valve. The material properties in the jacket of the container can be optimized in terms of "binding splinters together".

Using the RIM method, it is also possible to cover containers with a plastic sheathing after they have been closed with a valve. This becomes possible because the mold temperatures in the RIM method can be a great deal lower than in the conventional injection-molding system and, within the framework of the RIM system, the valve cannot be damaged by temperatures that are too high. Additionally, the mechanical forces associated with injection are lower, which also reduces the likelihood of valve damage.

Due to the lower mechanical load during coating, the use of the RIM method also makes it possible to use thinner glass inlets with wall thicknesses in the range of 0.7 – 1 mm with plastic sheathing strengths in the range of 1 – 2 mm, so that compressed-gas packages can be produced specifically for use in application devices (injection pen systems, for example) using this method.

Coating can also be carried out more economically using the RIM method. On the one hand, faster process times are possible, which increases throughput. On the other hand, the molds are less expensive, which also results in an economical production of small item counts.

It was determined, surprisingly, that the use of reactive polyurethane systems in the RIM method eliminates the need to pretreat the outer surface of the glass inlet to achieve optimal protection against splintering.

When using thermoplastics that are applied in the conventional injection molding system, it must be ensured by means of separate process steps, for example, that—as described in the cited publication DE 196 32 664 A1—the bond between plastic and glass surface is very weak, so that, if the container breaks, cracks in the glass inlet cannot spread into the plastic sheathing. When using reactive polyurethane systems according to the RIM method, the splinter-binding effect is independent of the load-bearing capacity of the bond between glass and plastic sheathing, so that previously-named process steps can be eliminated.

Using the RIM method, components that may be mechanically and thermally loaded only minimally can be coated by injection molding. This results in further possibilities for the production of compressed-gas packages for application systems.

Aerosol containers, a preferred application of the container according to the invention, typically have the shape of a small glass bottle having a volume between 5 ml and 125 ml.

Using the RIM method, it is also possible to coat glass containers having a volume of more than 125 ml and up to 2000 ml.

As a result, these containers can fulfill TRG 300 requirements for compressed-gas packages.

As a result of the measures according to the invention, it becomes possible to produce containers in which fluids contained therein can be safely sterilized using superheated steam (at 121° C or 134° C). Under these sterilization conditions, high pressures are produced in the closed vessel that, alone, would lead to the destruction of the vessel. Current glass laboratory bottles may therefore not be closed tightly when undergoing such a sterilization process, so that pressure compensation can take place. The plastic sheathing applied using the RIM method makes it possible, however, to optimize the glass inlet in terms of resistance to excess pressure and, in practical usage, it ensures safety if glass breaks.

Moreover, thermolabile inlets (thermoplastics, for example) are able to be coated.

The reactive-injection molding method itself is known. It is described in the following book, for instance:

> "Saschtiing, Hansjürgen. Kunststoff Taschenbuch,
> *[Plastics Handbook]*
> 24th Ed., published by Carl Hanser Verlag, Munich, Vienna, 1989,
> ISBN 3-446-15385-3"

Various method variants are known.

Polyurethane, polyamine, and polyurea systems, and thermosetting resins, are known in particular as reactively-vulcanizing plastics. Reference is made to the following book

"Domininghaus, Hans. Die Kunststoffe und ihre Eigenschaften, *[Plastics and Their Properties]* 4th Ed., published by VDI-Verlag GmbH, Düsseldorf, 1992"

for details.

The glass containers covered by injection molding—glass inlets—described are used preferably in the medical field. They can comprise various configurations. For instance, Figure 1 shows a partial longitudinal view of a glas inlet that is fillable with a medically effective substance sprayable as aerosol. A discharge opening having a crimp rim 2 is formed on the container sheathing 1, to which a metering valve can be attached. The base 3 bulges distinctly in the edge region 3a, having a flat center section 3b with a relatively small surface.

A plastic coating 4—which is shown in Figure 1 in an enlarged dimension and not in entirety—is applied to the glass inlet according to the reactive-injection molding system. The coating is applied in the base section 3 in such a fashion that a flat standing surface is produced over the cross-section of the glass container. In the upper section of the container, the coating extends to the rim of the discharge opening, i.e., it includes the crimp rim 2. Due to the lower mold temperatures in the reactive-injection molding method, however, the metering valve can also be placed on the crimp rim 2 before the coating is applied.

Preferably, however, the glass inlets are provided with a base 3' that bulges outward in entirety, as shown in Figure 2, because they can then withstand higher internal pressures.

The following relationship preferably exists for the base radius R, the container diameter D, and the dimension S of the outward bulge:

	min	max
S	1 mm	D/2
R	5 mm	D/2

Otherwise, the glass inlet according to Figure 2 is designed analogous in shape to the glass inlet according to Figure 1. Identical reference numerals are used for this reason.

Instead of a crimp rim, the glass inlets can also comprise a DIN glass thread GL 45 K for a screw-in stopper.

In addition to the medical field described, the glass containers can also be used to store sprayable cosmetic products and to store/prepare beverages.

The method according to the invention is also suited, therefore, to coat glass bottles for the production of carbonated mineral water when introducing CO_2 into tap water. The required pressure-loadability is thereby 12 bar, which indicates a TRG 300 test pressure of 18 bar. The volume of the bottles is typically 0.5 or 0.7 and 1.0 liter.